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CORROSION PRODUCT OF THE
TANTALUM - INTERSTITIAL OXYGEN - POTASSIUM
SYSTEM AT 1800° F (1255° K)

by C. William Hickam, Jr.

*Lewis Research Center
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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • DECEMBER 1967



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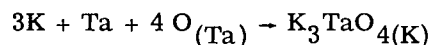
CORROSION PRODUCT OF THE TANTALUM - INTERSTITIAL OXYGEN - POTASSIUM SYSTEM AT 1800⁰ F (1255⁰ K)

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SUMMARY

Described herein are the isolation and identification of the corrosion product formed by the exposure of oxygen-doped tantalum to potassium. The corrosion of tantalum by liquid potassium appears to be quantitatively dependent on the oxygen impurity content and to occur by the formation of a ternary oxide. When tantalum containing oxygen in the range of 1600 to 3800 ppm is exposed to potassium at 1800⁰ F (1255⁰ K), depletion of oxygen from tantalum occurs and the hygroscopic potassium tantalate K_3TaO_4 is isolated as the reaction product. Indications are that, under the test conditions, the dissolution of tantalum is quantitatively governed by the equation:



These results imply that the total amount of "oxygen-effect" corrosion can be predicted when the total amount of interstitial oxygen in tantalum is known (i. e., oxygen in solution in the metal initially plus oxygen that enters the metal from the environment during the life of the system). Since oxygen-effect corrosion is the most serious type of corrosion encountered by tantalum alloys in contact with potassium at elevated temperatures, the present results are significant for the design and operation of advanced space power systems.

INTRODUCTION

The corrosion resistance of niobium and tantalum tubing alloys to alkali metals is of prime concern in the development of advanced space power systems (ref. 1). Indications are that susceptibility to alkali metal corrosion is a function of the system's oxygen content (refs. 2 to 5). This oxygen-effect corrosion is the most serious type of cor-

rosion encountered at elevated temperatures. It has been proposed (refs. 3 and 5) that oxygen reacts with an alkali metal such as potassium and a refractory metal M to form a ternary oxide:



This proposal is supported by two observations. First, oxygen distribution studies (ref. 2) indicate that oxygen migrates from niobium to potassium, contrary to the expected behavior based on the free energies of formation of the respective oxides. Second, corrosion products containing a refractory metal, oxygen, and an alkali metal have been found (refs. 2, 3, 5, and 6).

In the ground testing of space power systems, the main oxygen species likely to be present is interstitial oxygen, rather than a refractory metal oxide or an alkali metal oxide (ref. 1). Consequently, in this study of the reaction of a refractory metal, an alkali metal, and oxygen, the case of interstitial oxygen was investigated first. Reported herein are the results of tests in which tantalum specimens containing oxygen in the range of 1600 to 3800 ppm were exposed to potassium at 1800° F (1255° K) for 96 hours. Following exposure, the potassium was separated by distillation from the test specimen and the reaction product.

APPARATUS AND PROCEDURE

The experimental method employed for the identification of the corrosion product in the tantalum-oxygen-potassium system consisted of three steps. First, commercially pure tantalum wire with an oxygen content of 200 ppm was doped with oxygen to the range of 1600 to 3800 ppm. Second, the doped wire specimen was exposed to potassium at 1800° F (1255° K) for 96 hours. Third, potassium was removed by vacuum distillation, and the residue and the wire specimen were subjected to chemical and physical analysis.

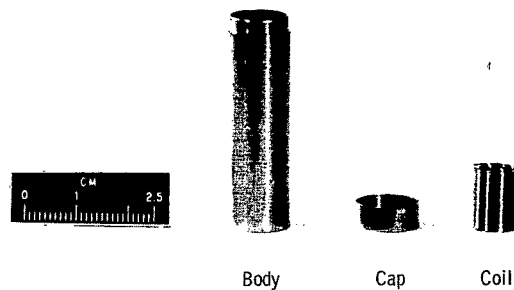
Oxygen Doping of Specimen

One-gram tantalum coils, made from 0.025-centimeter wire, were doped with oxygen at a pressure of approximately 10^{-5} torr ($\sim 10^{-3}$ N/m²) and at 1700° F (1200° K) in a vacuum apparatus similar to that described in reference 7. At this pressure, the doping time to obtain 3800-ppm oxygen, for example, was about 8 hours. The amount of oxygen added to the coils was measured by weight increase and checked by neutron activation or vacuum fusion analysis. The coils were examined for lattice expansion and possible

oxide formation by X-ray diffraction techniques. The X-ray diffraction pattern of a coil doped with 2720-ppm oxygen showed the absence of oxides, but the pattern of a coil which contained 3610-ppm oxygen showed the presence of TaO_2 . These results are in general agreement with reference 8, which reports the solubility of oxygen in tantalum to be 2680 ppm at 1000°C (1832°F). Calculations based on the diffusion rate of oxygen in tantalum at the doping temperature indicate that the rate is sufficient to ensure oxygen homogeneity in the tantalum coil.

Exposure of Specimen to Potassium

Tantalum capsules, 1.27 centimeters in diameter and 5 centimeters long, containing an oxygen-doped tantalum coil specimen (fig. 1) were loaded with 0.9 gram of potassium,



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Figure 1. - Test capsule and tantalum coil.

capped, and sealed by electron-beam welding in a special vacuum facility at a pressure of 10^{-5} torr (10^{-3} N/m²). (This procedure is described in Lewis motion picture C-241 entitled "Vacuum Handling of Space Power System Materials", which is available on loan. A description of the film and a request card are bound at the back of the report.) The potassium used contained less than 20 ppm of oxygen as analyzed by a mercury amalgamation method (ref. 9). The oxygen in the potassium accounted for less than 2 percent of the total available oxygen in the system.

Capsules were heated at 1800°F (1255°K) for 96 hours in a resistance-heated vacuum furnace (10^{-5} torr or 10^{-3} N/m²). Temperature gradients in the capsules were minimized by holding the capsules in a closely fitting molybdenum block.

Isolation and Identification of Reaction Product

The apparatus used to separate the reaction product from the potassium was a modification of the vacuum distillation apparatus described in reference 10. The modification consisted of the incorporation of capsule opening and transfer sections. Figure 2 shows a schematic representation of the product-separation apparatus. All operations in the apparatus were conducted at a vacuum level of 10^{-5} torr (10^{-3} N/m²) or less.

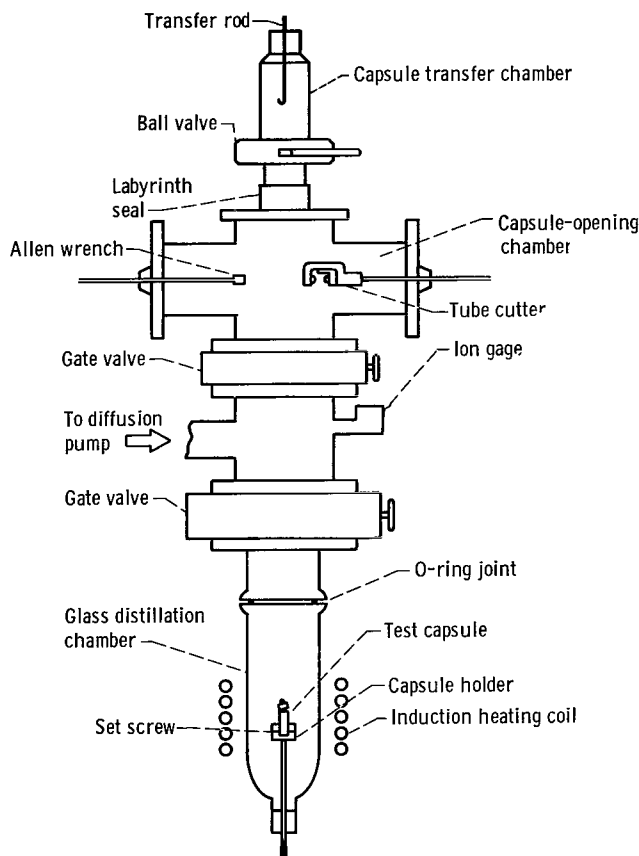


Figure 2. - Product separation apparatus.

Following exposure at test temperature, a test capsule was secured in the holder, the apparatus was evacuated, and the capsule was opened with the tube cutter. Potassium was removed by distillation at 600° F (589° K), and the capsule was transferred under vacuum to a dry box.

The corrosion product and the coil specimen were recovered for analysis in an argon-atmosphere dry box. Spectrometric (ref. 11) and flame photometric methods were used to determine tantalum and potassium, respectively, in the corrosion product. X-ray diffraction analyses were performed on the corrosion product and the coil specimen. Diffraction patterns were made with a Debye-Scherrer-type camera with an effective diameter of 11.46 centimeters.

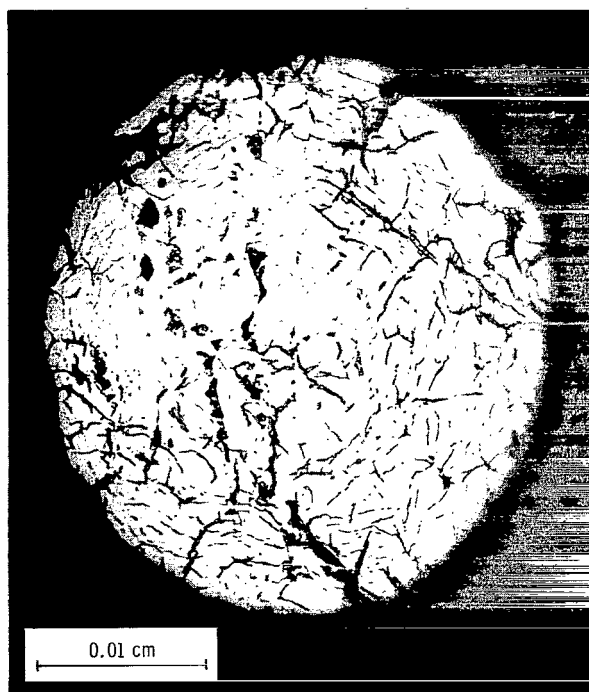
RESULTS

After test exposure to potassium, the lattice parameter of the tantalum coil specimens corresponded to that of pure tantalum (3.303 \AA or $3.303 \times 10^{-10} \text{ m}$) (refs. 8, 12, and 13). This correspondence indicated that the specimens had suffered complete oxygen depletion. The coil specimens fractured at the lightest touch. The cause of this behavior can be inferred from figure 3, which shows a typical specimen section following exposure to potassium. Extensive transgranular attack is evident.

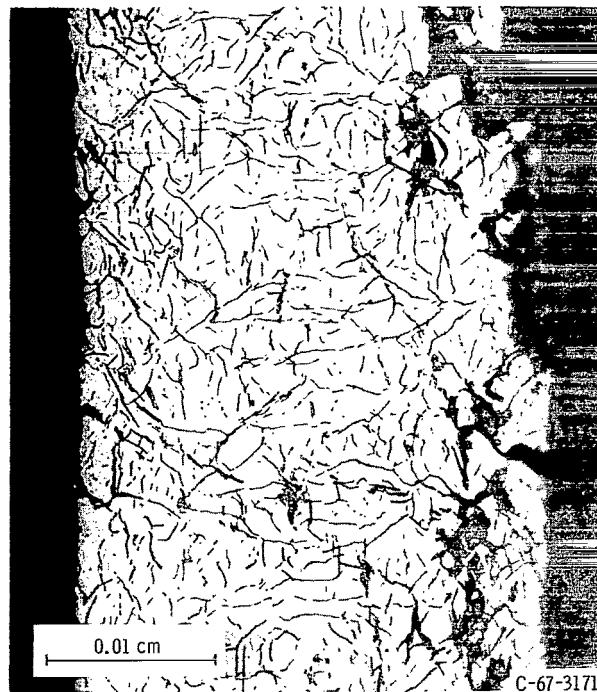
The corrosion product isolated was a hygroscopic crystalline solid. Table I presents the results of three tests for which the weight percents of potassium, tantalum, and oxygen were determined. These results are in agreement with those expected for the ternary oxide K_3TaO_4 . The X-ray diffraction pattern of a sample of the corrosion product from the third test corresponded closely to the pattern of the compound K_3TaO_4 given in reference 14. Both patterns are shown in table II. The high crystallinity of the corrosion product and the high radiation exposure (10 hr at 40 mA and 40 kV) used in this investigation probably account for points of variance with the published pattern, such as the additional lines and the intensity differences.

In a blank test, in which an undoped tantalum specimen was exposed to potassium, no corrosion product was detected. Based on the blank test and a consideration of the limits of detection of the analytical method used to determine tantalum (ref. 11), the solubility of tantalum in potassium at 1800° F (1255° K) is probably less than 10 ppm.

Another test was run to check the validity of a major assumption underlying the separation technique. The assumption is that the product formed at the reaction temperature (1800° F or 1255° K) would not alter during distillation at a much lower temperature (600° F or 589° K). Following exposure to potassium at 1800° F (1255° K) of a specimen containing 1150-ppm oxygen, the test capsule was opened, and the reaction product and the excess potassium were dissolved in butyl alcohol. The recovered wire specimen showed complete oxygen depletion. From a tantalum analysis of the alcohol solution and the assumption that the oxygen of the corrosion compound is equal to the oxygen initially in the test specimen, an oxygen to tantalum ratio of 4 was obtained. This ratio is in agreement with the oxygen to tantalum ratio of the ternary oxide K_3TaO_4 .



(a) Cross section.



(b) Longitudinal section.

Figure 3. - Typical etched section of tantalum wire after exposure to potassium.

TABLE I. - ANALYSIS OF CORROSION PRODUCT

Test	Potassium, wt percent	Tantalum, wt percent	Oxygen, wt percent	Oxygen in coil, ppm
1	29.9	49.5	^a 20.7	2800
2	32.4	51.2	^a 16.4	1600
3	32.1	49.4	^b 18.5	^c 3770
Average	31.5	50.0	18.5	----
Theoretical for K_3TaO_4	32.4	50.0	17.7	----

^aThe total corrosion product was analyzed. The weight of oxygen in the corrosion product was taken to be equal to the weight of oxygen initially in the tantalum specimen.

^bA 9.53-mg sample was analyzed. The weight of oxygen was determined by weight difference (i.e., the weight of the sample minus the combined weights of tantalum and potassium determined by chemical analysis).

^cX-ray diffraction pattern of pretest specimen indicated presence of tantalum suboxides.

TABLE II. - X-RAY POWDER DIFFRACTION PATTERN
OF CORROSION PRODUCT AND OF K_3TaO_4

Corrosion product		K_3TaO_4 (ref. 14)	
Interplanar distance, d, \AA (or $\times 10^{-10}$ m)	Intensity (a)	Interplanar distance, d, \AA (or $\times 10^{-10}$ m)	Intensity (a)
7.3	m		
6.5	vvw	6.36	vw
		6.10	vw
6.0	s	5.96	vw
5.4	s	5.32	m
5.1	s	5.03	vs(B)
		4.61	vw
4.27	w	4.27	w
4.15	vw	4.13	vvw
		4.02	vw
		3.92	vw
3.72	w	3.73	vvw
3.53	vw	3.54	vvw
3.37	vw		
3.20	vw	3.18	w
3.06	vs	3.06	s
2.99	vs	2.99	s
2.87	vs	2.88	m
2.79	vw	2.81	w
2.74	w		
2.56	m	2.56	vw
2.48	w		
2.40	s	2.40	w
2.27	vw		
2.22	vw		
2.17	vw		
2.12	vw		
2.07	vw		
2.01	w		
1.992	w		
1.951	m		
1.920	vvw		
1.897	m		
^b 1.883	m	1.88	vvw(B)

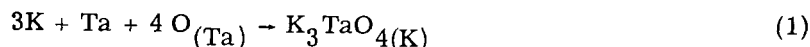
^aVery, very weak, vvw; very weak, vw; weak, w; medium, m; strong, s; very strong, vs; broad, B.

^bPlus 70 additional lines below 1.883 \AA .

DISCUSSION

Proposals that the corrosion intermediate in refractory metal - liquid-metal systems is a ternary oxide have been based mainly on experiments involving refractory metal oxides. Tyzack (ref. 6) has reported that when Nb_2O_5 is exposed to sodium at 600°C (1112°F), the reaction products are $\text{Na}_2\text{Nb}_2\text{O}_5$, niobium metal containing oxygen, and two unidentified compounds. Litman (ref. 2) reports that KNbO_3 and Nb_2O_5 result when niobium specimens covered with a NbO_2 - NbO scale are exposed to potassium at 815°C (1499°F) for 100 hours. No stoichiometry for the refractory metal oxide - alkali metal reaction is suggested by these investigators.

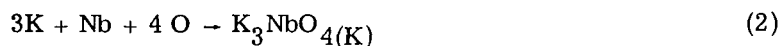
The identification and quantitative isolation of K_3TaO_4 in this study indicates that corrosion in the tantalum - interstitial oxygen - potassium system occurs by the reaction:



Equation (1) shows that knowing the amount of oxygen present (dissolved in tantalum) makes it possible to predict the amount of tantalum dissolution in potassium.

The prevalence of K_3TaO_4 as a reaction product, even when oxygen is present in a form other than interstitial oxygen, is suggested by the results of the third test. In this test about one-third of the total amount of oxygen initially contained in the specimen was in the form of tantalum suboxide. Nevertheless, the sole reaction product was K_3TaO_4 .

A further extension of the reaction given in equation (1) is present in the unpublished results of tests on the corrosion of niobium by potassium carried out by C. M. Scheuermann of the Lewis Research Center. From these tests a corrosion product was isolated which has a potassium to niobium atomic ratio of 3. Apparently, then, potassium corrosion of niobium in the presence of oxygen is similar to that of tantalum and can be represented by the following equivalent relation:



The reactions discussed previously may be used to account for two general findings concerning (1) solubility data for tantalum and niobium in potassium and (2) the corrosion resistance of gettered tantalum and niobium alloys in potassium.

First, solubility data for niobium and tantalum in potassium exhibit an inordinate variability. For example, the spread in solubility of niobium in potassium at 760°C (1400°F) is 40 to 410 ppm (ref. 5), and at 1000°C (1832°F) it is 15 to 171 ppm (ref. 15). An explanation for the variability of data can be made in terms of an uncontrolled test variable, namely, the oxygen content of the test specimen. As-received niobium or tantalum materials have widely differing amounts of oxygen impurity, depending

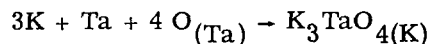
on their previous history of melting, working, and heat treatment. Also, significant oxygen contamination of the refractory metal can occur from the test environment during the course of a solubility test. Therefore, it is likely that the refractory metal specimens used contained unknown and widely varying amounts of oxygen. This possibility, in light of equations (1) and (2), would lead to a large variation in observed solubility. In any event, equations (1) and (2) suggest that, in future determinations, an explicit distinction be made between the actual solubility of niobium or tantalum in potassium and the oxygen-induced "apparent" solubility.

Second, tantalum and niobium alloys which contain an oxygen-gettering element (e.g., hafnium or zirconium) exhibit essentially no corrosion attack (ref. 3). This performance is a corollary of the reactions expressed in equations (1) and (2). If oxygen is unavailable, as is the situation when the getter element reacts with oxygen in the alloy to form a stable oxide, corrosion cannot occur by the formation and dissolution of a complex oxide. In the absence of oxygen, the remaining path for corrosion attack is direct solution of niobium or tantalum in potassium, a process of apparently low dissolution potential.

SUMMARY OF RESULTS

The corrosion of tantalum by liquid potassium appears to be quantitatively dependent on the amount of oxygen present in the tantalum and to occur by the formation of a ternary oxide. When tantalum was tested under the conditions of this study, 1600 to 3800 ppm oxygen in tantalum with potassium at 1800° F (1255° K), the hygroscopic potassium tantalate K_3TaO_4 was isolated as the reaction product. Complete depletion of oxygen from tantalum was observed.

These tests indicate the dissolution of tantalum to be governed by the equation:



This implies that the total amount of oxygen-effect corrosion can be predicted when the total amount of interstitial oxygen in tantalum is known. Since oxygen-effect corrosion is the most serious type of corrosion encountered by tantalum alloys in contact with potassium at elevated temperatures, these results are significant for the design and operation of advanced space power systems.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 7, 1967,
129-03-03-01-22.

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The film (16 mm, 12 min, color, sound) shows techniques to minimize contamination during the handling and testing of alkali and refractory metals. The two examples used to describe the techniques are (1) the determination of oxygen in alkali metal by vacuum amalgamation and (2) the preparation, welding, and testing of refractory metal - alkali metal corrosion capsules.

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